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(71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme  
von US): STOCKHAUSEN GMBH & CO. KG [DE/DE];  
Bakcrpfad 25, 47805 Krefeld (DE).

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(72) Erfinder; und  
(75) Erfinder/Anmelder (nur für US): FISCHER, Ul-  
rich [DE/DE]; Deutzer Str. 44, 41468 Neuss (DE).  
SCHROERS, Otto [DE/DE]; Dohrhofweg 1, 47803  
Krefeld (DE). WOEBEL, Wolfgang [DE/DE]; Lindenstr.  
9, 47877 Willich (DE).  
(74) Anwalt: KUTZENBERGER, Helga; Kutzenberger &  
Wolff, Theodor-Heuss-Ring 23, 50668 Köln (DE).

(54) Title: METHOD FOR THE PRODUCTION OF WATER-IN-WATER POLYMER DISPERSIONS

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON WASSER-IN-WASSER-POLYMERDISPERSIONEN

(57) Abstract: The invention relates to a method for the production of a water-in-water polymer dispersion, comprising polymer A and at least one polymer dispersing agent B, whereby monomers, distributed in an aqueous phase containing the water-soluble dispersion agent B, optionally with addition of a water-soluble salt, undergo a radical polymerisation. After said polymerisation a water-soluble acid is added to the water-soluble or water-absorbent polymer A, obtained as above, whereby the acid is added in amounts of 0.1-5 wt. % and the salt in amounts up to a maximum of 3.0 wt. %, each relative to the total dispersion, and the combined amount of acid and salt is a maximum of 5 wt. % relative to the total dispersion.

(57) Zusammenfassung: Die Erfindung betrifft Verfahren zur Herstellung einer Wasser-in-Wasser Polymerdispersion enthaltend Polymerisat A und wenigstens ein polymeres Dispergiermittel B, gemäß dem Monomere, die in einer wäßrigen Phase enthaltend das wasserlösliche Dispergiermittel B verteilt sind, ggf. Unter Zugabe eines wasserlöslichen Salzes einer radikalischen Polymerisation unterworfen werden und nach der Polymerisation zu dem so erhaltenen wasserlöslichen oder wasserquellbaren Polymerisat A eine wasserlösliche Säure zugesetzt wird, wobei die Säure in Mengen von 0,1-5 Gew.% und das Salz in Mengen bis maximal 3,0 Gew.%, jeweils bezogen auf die Gesamtdispersion, zugesetzt werden und die Gesamtmenge Salz und Säure maximal 5 Gew.%, bezogen auf die Gesamtdispersion, beträgt.

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(71) **STOCKHAUSEN GMBH & CO. KG,  
Bäkerpfab 25  
47805, KREFELD, XX (DE).**

(72) **WOEBEL, WOLFGANG (DE).  
SCHROERS, OTTO (DE).  
FISCHER, ULRICH (DE).**

(74) **BORDEN LADNER GERVAIS LLP**

(54) **PROCEDE DE PRODUCTION DE DISPERSIONS POLYMERES EAU-DANS-EAU**  
(54) **METHOD FOR THE PRODUCTION OF WATER-IN-WATER POLYMER DISPERSIONS**

(57)

The invention relates to a method for the production of a water-in-water polymer dispersion, comprising polymer A and at least one polymer dispersing agent B, whereby monomers, distributed in an aqueous phase containing the water-soluble dispersion agent B, optionally with addition of a water-soluble salt, undergo a radical polymerisation. After said polymerisation a water-soluble acid is added to the water-soluble or water-absorbent polymer A, obtained as above, whereby the acid is added in amounts of 0.1-5 wt. % and the salt in amounts up to a maximum of 3.0 wt. %, each relative to the total dispersion, and the combined amount of acid and salt is a maximum of 5 wt. % relative to the total dispersion.



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(71) Demandeur/Applicant:  
STOCKHAUSEN GMBH & CO. KG, DE  
(72) Inventeurs/Inventors:  
FISCHER, ULRICH, DE;  
SCHROERS, OTTO, DE;  
WOEBEL, WOLFGANG, DE  
(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : PROCEDE DE PRODUCTION DE DISPERSIONS POLYMERES EAU-DANS-EAU  
(54) Title: METHOD FOR THE PRODUCTION OF WATER-IN-WATER POLYMER DISPERSIONS

(57) Abrégé/Abstract:

The invention relates to a method for the production of a water-in-water polymer dispersion, comprising polymer A and at least one polymer dispersing agent B, whereby monomers, distributed in an aqueous phase containing the water-soluble dispersion agent B, optionally with addition of a water-soluble salt, undergo a radical polymerisation. After said polymerisation a water-soluble acid is added to the water-soluble or water-absorbent polymer A, obtained as above, whereby the acid is added in amounts of 0.1-5 wt. % and the salt in amounts up to a maximum of 3.0 wt. %, each relative to the total dispersion, and the combined amount of acid and salt is a maximum of 5 wt. % relative to the total dispersion.

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## **Abstract**

The invention relates to methods for manufacturing a water-in-water polymer dispersion containing polymer A and at least one polymeric dispersant B, according to which monomers, which are dispersed in an aqueous phase containing water-soluble dispersant B, are subjected to radical polymerisation, possibly following the addition of a water-soluble salt, and, after polymerisation, a water-soluble acid is added to the water-soluble and/or water-swellaable polymer A obtained in this way, where the acid is added in quantities of 0.1 to 0.5% by weight and the salt in quantities of up to a maximum of 3% by weight, each referred to the total dispersion, and the total quantity of salt and acid amounts to a maximum of 5% by weight, referred to the total dispersion.

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## **METHOD FOR THE PRODUCTION OF WATER-IN-WATER POLYMER DISPERSIONS**

The present invention relates to methods for manufacturing water-in-water polymer dispersions containing a finely dispersed, water-soluble or water-swellaable polymer A and a continuous, aqueous phase containing a polymeric dispersant B, the water-in-water polymer dispersions obtainable in this way and their use as auxiliaries in papermaking or as flocculants in the sedimentation of solids.

The manufacture of water-in-water polymer dispersions is described repeatedly in the prior art. The main target in this context is to obtain water-in-water dispersions that are easier to handle. Thus, it is known from international application WO 98/14405 that the addition of a mixture of a cosmotropic and a chaotropic or an anionic, organic salt during the manufacture of the dispersed polymer component is capable of lowering the viscosity of the water-in-water dispersions.

International application WO 98/31748 describes water-in-water dispersions which are stable and, despite a relatively high content of dispersed polymers, pourable, provided that, during production of the water-in-water dispersions, a water-soluble, inorganic salt is added to the dispersed monomer solution in quantities of at least 10% by weight prior to polymerisation. High salt quantities of this kind are not acceptable for some applications of water-in-water dispersions.

International application WO 98/31749 describes water-in-water dispersions which remain pourable and display no irreversible agglomeration in storage, provided that the water-in-water dispersions are already pourable after their production on account of their low viscosity. According to the teaching of this international application, this is achieved in that a polyhydroxy compound is added to the dispersion medium in which the monomer solution to be polymerised is present. However, when being further diluted, the water-in-water dispersions obtained, which may possibly also contain salts, must be diluted beyond a certain degree, because an undesirably great increase in the Brookfield viscosity otherwise occurs during dilution compared to the undiluted water-in-water dispersion. This is, however, disadvantageous for the application of the water-in-water dispersions.

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European application EP-A-0 630 909 describes a method for manufacturing water-in-water dispersions, according to which a polyvalent, anionic salt is added to the dispersed monomer solution to be polymerised in quantities of at least 15% by weight for viscosity control. More salt is added to reduce the viscosity of the water-in-water dispersions obtained. Again, the large quantity of salt added means that the water-in-water dispersions cannot be used without difficulty for every application.

Moreover, in the case of the water-in-water dispersions known from the prior art, prolonged storage, especially under extreme conditions, such as temperatures of over 25 °C to 50 °C, can result in changes, i.e. impairments of the advantageous properties of water-in-water dispersions, which lead to longer drainage times, for example.

Consequently, the object of the present invention was to provide a method by which water-in-water polymer dispersions are obtained that display virtually unchanged service properties even after storage under extreme conditions, such as temperatures of over 25 °C to 50 °C

According to the invention, this is achieved by providing a method for manufacturing a water-in-water polymer dispersion containing a water-soluble and/or water-swellaible polymer A and a polymeric, water-soluble dispersant B, according to which the monomers, which are dispersed in an aqueous phase containing water-soluble dispersant B, are subjected to radical polymerisation, possibly following the addition of a water-soluble salt, and, after polymerisation, a water-soluble acid is added to the water-in-water dispersion obtained in this way, which is characterised in that the acid is added in quantities of 0.1 to 0.5% by weight, the salt in quantities of up to a maximum of 3% by weight, each referred to the total dispersion, and the acid and the salt together are added in quantities of a maximum of 5% by weight, referred to the total dispersion.

The acid is preferably added in quantities of 0.2 to 3.5% by weight, particularly preferably in quantities of 0.3 to 2% by weight, referred to the total dispersion.

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Insofar as a salt is used in manufacturing the water-in-water polymer dispersion, this salt is preferably added in quantities of up to a maximum of 2.0% by weight, particularly preferably in quantities of 0.5 to 1.5% by weight, referred to the total dispersion. In this context, the quantities of added water-soluble acid and possibly added water-soluble salt should preferably amount to a maximum of 3.5% by weight, referred to the total dispersion.

Water-soluble organic acids and/or inorganic acids can be used as the acid added to the water-in-water polymer dispersions manufactured according to the invention. Particularly suitable for use as organic, water-soluble acids are carboxylic acids, sulphonic acids, phosphonic acids, preferably aliphatic or aromatic monocarboxylic, dicarboxylic, polycarboxylic acids and/or hydroxycarboxylic acids, preferably acetic acid, propionic acid, citric acid, oxalic acid, succinic acid, malonic acid, adipic acid, fumaric acid, maleic acid, benzoic acid, most particularly preferably citric acid, adipic acid and/or benzoic acid. Suitable for use as inorganic acids are water-soluble mineral acids, preferably hydrochloric acid, sulphuric acid, nitric acid and/or phosphoric acid. Citric acid, adipic acid, benzoic acid, hydrochloric acid, sulphuric acid and/or phosphoric acid is used with particular preference.

In order to implement the methods according to the invention, the monomers, preferably in the form of an aqueous monomer solution, are finely dispersed in an aqueous phase containing at least one polymeric dispersant B. These polymeric dispersants have a relatively low molecular weight and preferably display an average molecular weight  $M_w$  of max.  $2.0 \times 10^6$ , preferably 50,000 to  $1.2 \times 10^6$  g/mol, as measured by the GPC method (gel permeation chromatography with 1.5% formic acid as eluent against pullulan standards).

These polymeric dispersants display at least one functional group selected from the range of ether, carboxyl, sulfo, sulphate ester, amino, amido, imido, tert. amino and/or quaternary ammonium groups.

Cellulose derivatives, polyvinyl acetates, starch, starch derivatives, dextrans, polyvinylpyrrolidones, polyvinylpyridines, polyethylene imines, polyamines, polyvinylimidazoles, polyvinylsuccinimides, polyvinyl-2-methylsuccinimides, polyvinyl-

1,3-oxazolidone-2, polyvinyl-2-methylimidazolines and/or their respective copolymers with maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, (meth)acrylic acid, salts of (meth)acrylic acid and/or (meth)acrylic amide compounds can be mentioned as examples of these.

Particularly preferably used as polymeric dispersants B are cationic polymers that are made up of at least 30% by weight, preferably at least 50% by weight, particularly preferably 100% by weight, cationic monomer units derived from cationic, ethylenically unsaturated monomers, such as diallyldimethylammonium chloride, dialkylaminoalkyl(meth)acrylate or acrylamide with 1 to 3 C atoms in the alkyl or alkylene groups and protonated or quaternised into ammonium salts, preferably methyl chloride-quaternised ammonium salts of dimethylaminoethyl(meth)acrylate, dimethylaminopropyl(meth)acrylate, dimethylaminopropyl(meth)acrylamide, dimethylaminohydroxypropyl(meth)acrylate. Polydiallyldimethylammonium chloride is used with particular preference as the polymeric dispersant B in the method according to the invention.

In a preferred embodiment of the methods according to the invention, the water-soluble, polymeric dispersant B is used together with a water-soluble, polyfunctional alcohol and/or the product of its reaction with fatty amines. Particularly suitable in this context are polyalkylene glycols, preferably polyethylene glycols, polypropylene glycols, block copolymers of propylene/ethylene oxide, with molecular weights of 50 to 50,000, preferably 1,500 to 30,000, low-molecular polyfunctional alcohols, such as glycerin, ethylene glycol, propylene glycol, pentaerythritol and/or sorbitol as polyfunctional water-soluble alcohols, and/or the products of their reaction with fatty amines with C<sub>6</sub>-C<sub>22</sub> in the alkyl or alkylene residue.

The aqueous phase in which the monomers are dispersed, preferably in the form of an aqueous solution, must contain sufficient water-soluble polymeric dispersant B and, if applicable, polyfunctional alcohol and/or the reaction product mentioned for the polymer A formed during polymerisation to remain dispersed and to prevent uncontrolled growth of the polymer particles and/or agglomeration of the polymer particles formed. Polymeric dispersant B and the other dispersant components

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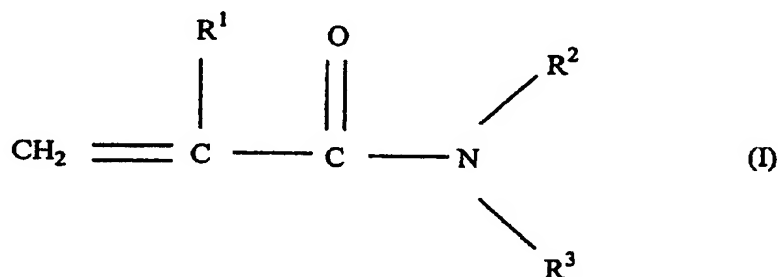
possibly present are preferably added in quantities of 5 to 50% by weight, preferably 10 to 20% by weight, referred to the total dispersion.

If additional water-soluble dispersant components are used along with polymeric dispersant B, a weight ratio of polymeric dispersant B to these components of 1:0.01 to 0.5, preferably 1:0.01 to 0.3, should be maintained.

The monomers present in the aqueous phase containing polymeric dispersant B in dispersed form, preferably in finely and homogeneously dispersed form, comprise cationic and/or amphiphilic, ethyleneically unsaturated monomers, where their possibly present content of water-insoluble monomers is selected such as not to impair the water-solubility or water-swellability of polymer A obtained after polymerisation.

Polymers A manufactured by the method according to the invention are high-molecular, but nonetheless water-soluble or water-swellable polymers with an average molecular weight of  $M_w$ , as measured by the GPC method, of  $> 1.0 \times 10^6$  g/mol, where the average molecular weight  $M_w$  of polymer A is always greater than that of polymeric dispersant B.

Compounds of the following general formula (I) can be used as non-ionic monomers for manufacturing polymers A:

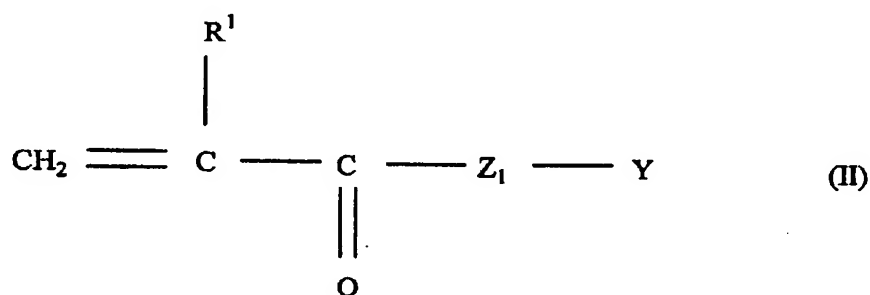


where

$\text{R}^1$  stands for hydrogen or a methyl residue, and  
 $\text{R}^2$  and  $\text{R}^3$  stand, independently of each other, for hydrogen, for an alkyl or hydroxyalkyl residue with 1 to 5 C atoms.

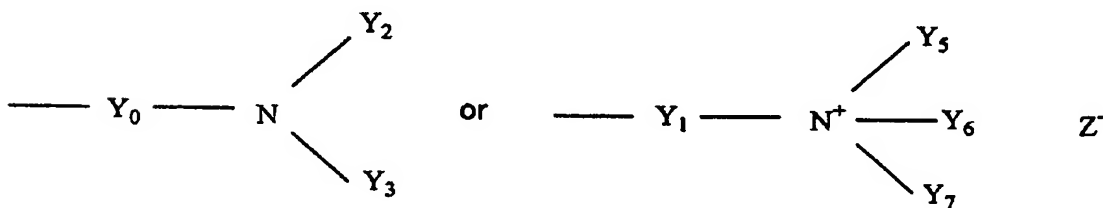
(Meth)acrylamide, N-methyl(meth)acrylamide, N-isopropyl(meth)acrylamide or N,N-substituted (meth)acrylamides, such as N,N'-dimethyl(meth)acrylamide, N,N'-diethyl(meth)acrylamide, N-methyl-N-ethyl(meth)acrylamide or N-hydroxyethyl(meth)acrylamide, is preferably used, most particularly preferably acrylamide.

Compounds of the following general formula (II) are suitable as cationic monomers for manufacturing polymers A:



where

- $\text{R}^1$  stands for hydrogen or a methyl residue,  
 $\text{Z}_1$  stands for O, NH or  $\text{NR}_4$  with  $\text{R}_4$  for an alkyl residue with 1 to 4 C atoms, and  
 $\text{Y}$  for one of the groups



and

where

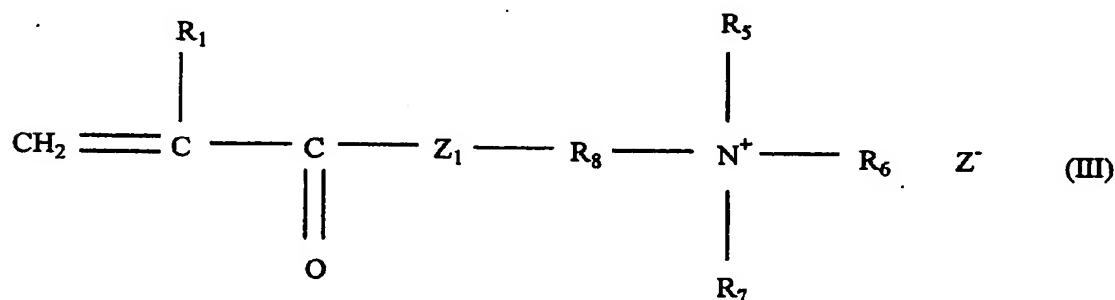
$\text{Y}_0$  and  $\text{Y}_1$  stand for an alkylene residue, possibly substituted with OH groups, with 2 to 6 C atoms,

$Y_2, Y_3, Y_4, Y_5, Y_6, Y_7$ , independently of each other, stand for an alkyl residue with 1 to 6 C atoms, and

$Z^-$  stands for halogen, acetate,  $SO_4CH_3^-$ .

Protonated or quaternised dialkylaminoalkyl(meth)acrylates or dialkylaminoalkyl(meth)acrylamides with  $C_1$  to  $C_3$  in the alkyl or alkylene groups are preferably suitable, particularly preferably the methyl chloride-quaternised ammonium salt of dimethylaminoethyl(meth)acrylate, dimethylaminopropyl(meth)acrylate, dimethylaminoethyl(meth)acrylate, diethylaminoethyl(meth)acrylate, dimethylaminomethyl(meth)acrylate, dimethylaminoethyl(meth)acrylamide and/or dimethylaminopropyl(meth)acrylamide.

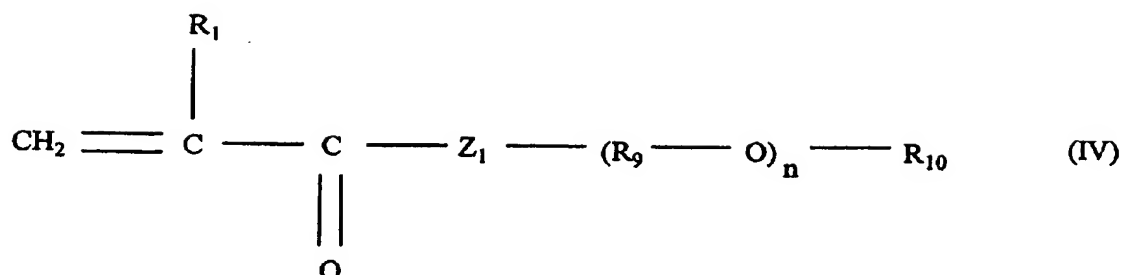
Compounds of the following general formula (III) or (IV) are suitable as amphiphilic monomers:



where

- $Z_1$  stands for O, NH or  $NR_4$  with  $R_4$  for alkyl with 1 to 4 carbon atoms,
- $R_1$  stands for hydrogen or a methyl residue,
- $R_8$  stands for alkylene with 1 to 6 carbon atoms,
- $R_5$  and  $R_6$  stand, independently of each other, for an alkyl residue with 1 to 6 carbon atoms,
- $R_7$  stands for an alkyl, aryl and/or aralkyl residue with 8 to 32 carbon atoms, and
- $Z^-$  stands for halogen, pseudo-halogen,  $SO_4CH_3^-$  or acetate

or



where

- $\text{Z}_1$  stands for O, NH or  $\text{NR}_4$  with  $\text{R}_4$  for alkyl with 1 to 4 carbon atoms,  
 $\text{R}_1$  stands for hydrogen or a methyl residue,  
 $\text{R}_{10}$  stands for hydrogen, an alkyl, aryl and/or aralkyl residue with 8 to 32 carbon atoms,  
 $\text{R}_9$  stands for an alkylene residue with 2 to 6 carbon atoms,  
 and  
 $n$  stands for an integer between 1 and 50.

These are preferably conversion products of (meth)acrylic acid with polyethylene glycols (10 to 40 ethylene oxide units) that have been etherified with fatty alcohol, or the corresponding conversion products with (meth)acrylamide.

For manufacturing polymer A, a monomer composition is preferably selected which consists of 1 to 99% by weight, preferably 20 to 80% by weight, cationic monomers, referred in each case to the total quantity of monomer. Particularly preferably, polymer A is manufactured using a mixture of non-ionic monomers, preferably acrylamide, and cationic monomers of general formula II, preferably quaternised dialkylaminoalkyl(meth)acrylates and/or dialkylaminoalkyl(meth)acrylamides. Most particularly preferably, dimethylaminoethyl(meth)acrylate quaternised with methyl chloride is used. In monomer mixtures of this kind, the content of cationic monomers is preferably at least 20%.

Referred to the total solution or to the resultant total dispersion, the monomers are dispersed in quantities of 5 to 60% by weight, preferably 10 to 50% by weight, in the aqueous phase, which contains at least one dispersant B. High-molecular polymer A is formed from the monomers by polymerisation.

Polymeric dispersant B and polymer A are different, where this difference can be a result of physical parameters, such as different molecular weights and/or chemical structures, or of different monomer compositions.

In the method according to the invention, polymerisation is preferably performed in the presence of a water-soluble salt. Ammonium, alkaline metal and/or alkaline-earth metal salts can be used as the water-soluble salt, preferably ammonium, sodium, potassium, calcium and/or magnesium salts. Salts of this kind can be salts of an inorganic acid or an organic acid, preferably of an organic carboxylic acid, sulphonic acid or phosphonic acid, or of a mineral acid. The water-soluble salts are preferably salts of an aliphatic or aromatic monocarboxylic, dicarboxylic or polycarboxylic acid, a hydroxycarboxylic acid, preferably acetic acid, propionic acid, citric acid, oxalic acid, succinic acid, malonic acid, adipic acid, fumaric acid, maleic acid or benzoic acid or sulphuric acid, hydrochloric acid or phosphoric acid. Most particularly preferably, sodium chloride, ammonium sulphate and/or sodium sulphate are used as water-soluble salts.

The salt can be added to the system before polymerisation, during polymerisation or after polymerisation. Addition of the salt before polymerisation of the monomers is preferred.

Following polymerisation, a water-soluble acid is added to the water-in-water polymer dispersion in quantities of 0.1 to 5% by weight, preferably in quantities of 0.2 to 3.5% by weight, particularly preferably in quantities of 0.3 to 2.0% by weight, referred in each case to the total dispersion. Addition is preferably performed while stirring. Suitable water-soluble acids are organic acids and/or inorganic acids, preferably organic carboxylic acids, sulphonic acids, phosphonic acids or mineral acids.

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Preferably suitable as organic acids are carboxylic acids, such as aliphatic or aromatic monocarboxylic, dicarboxylic, polycarboxylic acids and/or hydroxycarboxylic acids, preferably acetic acid, propionic acid, citric acid, oxalic acid, succinic acid, malonic acid, adipic acid, fumaric acid, maleic acid, benzoic acid, particularly preferably citric acid, adipic acid and/or benzoic acid, while hydrochloric acid, sulphuric acid and/or phosphoric acid are preferably suitable as inorganic acids. Citric acid, adipic acid and/or benzoic acid are particularly preferred.

In order to implement the method according to the invention, the continuous aqueous phase is produced by dissolving or diluting polymeric dispersant B, possibly a polyfunctional alcohol and/or a corresponding product of conversion with fatty amines, in water and dispersing the monomers or their aqueous solution by known dispersion methods, preferably by stirring.

The monomers of polymer A can be incorporated into the continuous aqueous phase either directly as such or preferably in the form of an aqueous monomer solution.

The monomer solution generally contains 5 to 60% by weight, preferably 10 to 50% by weight, monomers, referred to the total solution, while the remainder consists of water and any auxiliaries contained therein, such as chelating agents. Polymerisation is started, for example, by means of radical initiators referred to as polymerisation initiators. The radical initiators used are preferably azo compounds, such as 2,2-azobisisobutyronitrile, 2,2-azobis(2-amidino-propane)dihydrochloride or, preferably, potassium persulphate, ammonium persulphate, hydrogen peroxide, possibly in combination with a reducing agent, such as an amine or sodium sulphite. Referred to the monomers to be polymerised, the quantity of initiator is generally in the region of  $10^{-3}$  to 1% by weight, preferably  $10^{-2}$  to 0.1% by weight. The initiators can either be added completely at the start of polymerisation, or also only partly with subsequent addition of the remainder throughout the course of polymerisation. Similarly, the monomers or the monomer solution can be completely or partly dispersed in dispersant B at the start of polymerisation, in which case the remainder of the monomers or the monomer solution is added in metered partial quantities or as a continuous stream distributed over the entire course of polymerisation. Moreover, it is also possible to manufacture the water-in-water dispersions in accordance with the

method in EP-A-0 664 302, the corresponding disclosure of which is herewith introduced as a reference. Essentially, this procedure involves the removal of water being during polymerisation and, if necessary, the addition of polymeric dispersant B.

The polymerisation temperature is generally 0 to 120 °C, preferably 50 to 90 °C. Polymerisation is preferably performed in such a way that the system is flushed with inert gas and polymerisation takes place in an inert-gas atmosphere, e.g. in a nitrogen atmosphere. The polymerisation conversion or the end of polymerisation can easily be ascertained by determining the residual monomer content. The methods for doing this are known to a person skilled in the art.

Following polymerisation, it may be advantageous to cool the reaction mixture before the acid is added, preferably while stirring the dispersion.

The method according to the invention succeeds in producing water-in-water dispersions within generally short manufacturing times.

The water-in-water polymer dispersions obtainable according to the invention have the unexpected advantage that, not only after production, i.e. before being stored for any length of time, and possibly after dilution with water, they are excellent flocculants in the sedimentation of solids, preferably in the conditioning of water and process water or the treatment of waste water or in the extraction of raw materials, preferably of coal, aluminium or petroleum, auxiliaries in papermaking or demulsifiers in the separation of water mixtures containing oil and/or grease, excellent thickeners, retention agents and drainage aids in papermaking and/or additives for crop protection products, possibly together with other biologically effective substances, or anti-erosion agents. The water-in-water dispersions obtainable according to the invention display virtually no change in this excellent efficacy even after lengthy storage under extreme conditions, e.g. at elevated temperatures, i.e. temperatures of more than 25 °C and up to a maximum of 50 °C. This preservation of quality of the dispersions obtainable according to the invention is a hitherto unfulfilled demand of users in industry and indispensable if, among other things, these dispersions are to be transported to, and used in, regions subject to extreme climatic conditions.

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## Methods

### 1. Determination of the solution viscosity

To determine the solution viscosity of the water-in-water dispersions manufactured according to the invention, a 5% by weight solution in fully demineralised water is prepared, referred to the water-in-water polymer dispersion. 340 g of the 5% solution are required for the measurement. To this end, the necessary quantity of fully demineralised water is placed in a 400 ml beaker. The water in the beaker is then stirred with a finger agitator so vigorously that a vortex forms that reaches down to the bottom of the beaker. The amount of water-in-water dispersion required to prepare the 5% solution is added to the agitated water in the beaker as a single dose using a disposable syringe. The solution is then stirred for 1 hour at 300 rpm ( $\pm 10$  rpm). After standing for 10 minutes, the Brookfield viscosity is determined with the help of an RVT-DV II Brookfield viscometer using a No. 2 spindle at speed 10.

### 2. Determination of the salt viscosity

289 g fully demineralised water are weighed into a 400 ml beaker. The water in the beaker is then stirred with a finger agitator so vigorously that a vortex forms that reaches down to the bottom of the beaker. 17 g of the water-in-water dispersion prepared according to the invention are added to the agitated water in the beaker as a single dose using a disposable syringe. Once the water-in-water dispersion has dissolved, 34 g sodium chloride (technical) are strewn in. The solution is stirred for 60 minutes at  $300 \pm 10$  rpm and then left to stand for another 10 minutes. The Brookfield viscosity is subsequently determined with the help of an RVT-DV II Brookfield viscometer using a No. 1 spindle at speed 10.

### 3. Determination of the flocculation value using Stammberge slurry

This method is used to determine the sedimentation time required by the flocculated solid during solid/liquid separation by sedimentation to sediment through a defined stretch of the liquid column. For implementation of the method, refer to the publication by J. Reuter in "Umwelt" 1/1981, pages 25 to 27.



A dispersion of the following substances is first prepared for the measurement:

The solid used is "Blauton HFF-Spezial", approx. 37%  $\text{Al}_2\text{O}_3$  > 95% under 2  $\mu\text{m}$  (Tonwerke Braun Witterschlick / Bonn), which is dispersed in Krefeld tap water (or synthetic tap water of 25° German hardness).

To this end, 18 g Blauton are added to 1000 ml tap water.

The mixture is then dispersed with a mixer ( $10,000 \pm 100$  rpm ) for 20 seconds.

The resultant dispersion is poured into a standardised test cylinder (see Figure 1) up to the top mark.

The test cylinder has two marks 40 mm apart, is made of plexiglass and holds 250 ml up to the top mark. The numbers in Figure 1 are in millimetres.

Preparation of the water-in-water dispersion for determination of the flocculation value:

The water-in-water dispersions to be tested are diluted with tap water to a polymer content of 0.01% by weight in accordance with their polymer content (polymer A and polymeric dispersant B).

In order to measure the flocculation value, the test cylinder filled with the clay dispersion described above is placed under a finger agitator.

While stirring (320 rpm), 2.5 ml aluminium sulphate solution ( $200 \text{ g Al}_2(\text{SO}_4)_3 \times 18 \text{ H}_2\text{O}$ /litre distilled water) are added, after which 5 ml of the 0.01% polymer solution described above are added within 15 seconds and the agitator is switched off after a further 5 seconds. This now gives rise to flocculation (agglomeration) of the clay dispersion, which settles rapidly. Measurement of the time is started once the clay flocs have reached the upper (first) mark on the test cylinder. The time taken to reach the lower (second) mark is referred to as the flocculation value in seconds.

The smaller the flocculation value, the more advantageous the effect of the flocculant.

4. Determination of drainage acceleration using a Schopper-Riegler beating and freeness tester

This test method is described by H. Becker and D. Zerler in the "Schriftenreihe der Papiermacherschule", Vol. 15, first edition 1995, pp. 68 to 71.

According to this test method, the acceleration of drainage resulting from the addition of water-in-water dispersions to defined pulp suspensions is determined with the help of a Schopper-Riegler beating and freeness tester (Haage).

To this end, water-in-water dispersions are adjusted to a polymer content (polymer A and polymeric dispersant B) of 0.01% by weight, using fully demineralised water in each case. The drainage apparatus used is the above-mentioned Schopper-Riegler apparatus, which comprises a 2000 ml metal cup with a wire on the underside which is sealed off with a cone during filling.

The acceleration of drainage is determined on a 1% by weight pulp suspension made of standard recovered paper.

To this end, 3 g oven-dry recovered paper fibres are adjusted with tap water to 300 g of a 1% by weight pulp suspension in the Schopper-Riegler freeness cup. The drainage accelerating agent described above, consisting of a water-in-water dispersion, is adjusted to a 0.01% by weight solution. The drainage tests are performed with 3 polymer concentrations, where 3 ml, 6 ml and 9 ml of the 0.01% drainage agent are each diluted with 200 ml tap water and this solution is added to the paper fibre suspension in the Schopper-Riegler freeness cup and made up to 1000 ml with tap water in each case. The contents of the cup are then transferred to the filling chamber of the Schopper-Riegler apparatus, which is closed at the bottom, and the sealing cone is immediately unlocked. The time is measured that is required to filter off 700 ml of the 1000 ml paper fibre suspension after opening the sealing cone. To this end, the filtrate is collected and the time taken to reach 700 ml recorded. This time is referred to as the drainage time.

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## Examples

In the following examples, the solution viscosity or salt viscosity, the flocculation value and the drainage effect were determined in accordance with the methods described above. The term "solution" is always taken to mean an aqueous solution.

### Example 1

231.0 g acrylamide solution (50%), 231.1 g fully demineralised water, 43.2 g dimethylaminoethylacrylate quaternised with methyl chloride (80%), 9.5 g technical ammonium sulphate, 0.2 g of the sodium salt of diethylenetriamine pentaacetic acid (40%), 400 g polydiallyldimethylammonium chloride (40%), 14.25 g polyethylene glycol with a molecular weight of 9,000 to 12,000 and 5 g 2,2-azobis(2-amidinopropane)dihydrochloride are put into a 2 l flask fitted with an agitator, a nitrogen supply line and a connection to a vacuum pump and dispersed homogeneously by stirring. The flask is deaerated for approx. 10 minutes by connecting it to a vacuum pump and the mixture is then blown out with nitrogen for approx. 15 minutes in order to remove the remaining oxygen. While stirring at 100 to 150 rpm, the mixture is heated to 35 °C in order to polymerise the monomers. Once a maximum temperature of 75 °C has been reached, the mixture is briefly re-stirred for 15 minutes. Subsequently, 10 g citric acid in fine powder form are strewn in and mixed with the dispersion by stirring. After 20 minutes of constant stirring, the water-in-water dispersion obtained is cooled to 20 °C.

The solution viscosity of the water-in-water dispersion was determined as being 60 mPa · s, as described above. The salt viscosity was 36 mPa · s, again as described above.

### Comparative example 1

Example 1 was repeated, with the difference that citric acid was not added at any time.

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The 5% solution viscosity of the water-in-water dispersion thus obtained was determined, as described above, as being 52 mPa · s and the salt viscosity as being 32 mPa · s.

#### Example 2

231.0 g acrylamide solution (50%), 231.1 g fully demineralised water, 43.2 g dimethylaminoethylacrylate quaternised with methyl chloride (80%), 9.5 g technical ammonium sulphate, 0.2 g of the sodium salt of diethylenetriamine pentaacetic acid (40%), 400 g polytrimethammoniumpropylacrylamide chloride (40%), 14.25 g polyethylene glycol with a molecular weight of 9,000 to 12,000 and 4 g 2,2-azobis(2-amidinopropane)dihydrochloride are put into a 2 l flask fitted with an agitator, a nitrogen supply line and a connection to a vacuum pump and dispersed by stirring. The flask is deaerated for approx. 10 minutes by connecting to a vacuum pump and the mixture is then blown out with nitrogen for approx. 15 minutes in order to remove the remaining oxygen. While stirring at 100 to 150 rpm, the mixture is heated to 35 °C in order to polymerise the monomers. Once a maximum temperature of 76 °C has been reached, the mixture is briefly re-stirred for 15 minutes. Subsequently, 10 g citric acid in fine powder form are strewn in and mixed with the dispersion by stirring. After 35 minutes of constant stirring, the water-in-water dispersion obtained is cooled to 20 °C.

The solution viscosity of the water-in-water dispersion was determined as being 300 mPa · s, as described above. The salt viscosity was 150 mPa · s, again as described above.

#### Comparative example 2

Example 2 was repeated, except that citric acid was not added at any time.

The 5% solution viscosity of the water-in-water dispersion thus obtained was determined, as described above, as being 280 mPa · s and the salt viscosity, as described above, as being 135 mPa · s.

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### Example 3

163.2 g fully demineralised water, 144.75 g 80% by weight trimethylammonium ethylacrylate chloride, 231.0 g 50% by weight acrylamide solution, 420.0 g 40% by weight polydiallyldimethylammonium chloride with a viscosity of the aqueous solution in the range of 200 to 400 mPas, 14.0 g polyethylene glycol with a molecular weight in the range of 9,000 to 12,000, 12.2 g technical ammonium sulphate, 0.26 g 40% by weight diethylenetriamine valeric acid sodium salt and 1.54 g 2,2-azobis(2-amidinopropane)dihydrochloride are put into a 2 l flask fitted with an agitator, a nitrogen supply line and a connection to a vacuum pump.

The pH value of the solution is 5.0. The solution is freed of oxygen and polymerised in accordance with the procedure specified in Example 1. After a maximum temperature of 82 °C has been reached, 12.85 g fine citric acid powder are mixed into the water-in-water dispersion by stirring, as described in Example 1, and the dispersion is then cooled to 20 °C while stirring constantly. The polymer content of the dispersion is 39.9% by weight.

The dispersion has a solution viscosity of 730 mPas and a salt viscosity of 210 mPas. A salt viscosity of 214 mPas is determined after storing the dispersion for a period of 60 days at a temperature of 40 °C.

### Comparative example 3

Example 3 was repeated, but without adding citric acid at any time.

The dispersion thus obtained has a solution viscosity of 700 mPas and a salt viscosity of 190 mPas. A salt viscosity of 136 mPas is determined after storage of the dispersion for a period of 60 days at a temperature of 40 °C, this corresponding to a decrease of 28.4% referred to the value after preparation of the dispersion.

#### Example 4

272.6 g fully demineralised water, 66.9 g 80% by weight trimethylammonium ethylacrylate chloride, 321.0 g 50% by weight acrylamide solution, 310.0 g 40% by weight polytrimethylammoniumpropylacrylamide chloride with a viscosity of the aqueous solution in the range of 150 to 300 mPas, 20.0 g technical ammonium sulphate, 2.0 g 5% by weight diethylenetriamine valeric acid sodium salt and 0.5 g 2,2-azobis(2-amidinopropane)dihydrochloride are put into a 2 l flask fitted with an agitator, a nitrogen supply line and a connection to a vacuum pump.

The solution is freed of oxygen, heated to 40 °C and polymerised in accordance with the procedure specified in Example 1. After a maximum temperature of 86 °C has been reached, 5.0 g fine citric acid powder are mixed into the water-in-water polymer dispersion by stirring and the dispersion is then cooled to 20 °C while stirring constantly. The polymer content of the dispersion is 33.8% by weight.

The dispersion has a solution viscosity of 564 mPas and a salt viscosity of 248 mPas. The solution viscosity is 308 mPas after storage of the dispersion for a period of 55 days at a temperature of 50 °C, this corresponding to a decrease of 45.4% referred to the value after preparation of the dispersion.

#### Example 5

A water-in-water polymer dispersion is prepared as in Example 4, except that the monomer solution contains 267.6 g water and 10.0 g fine citric acid powder are added after polymerisation.

The dispersion has a solution viscosity of 548 mPas and a salt viscosity of 227 mPas. The solution viscosity is 336 mPas after storage of the dispersion for a period of 55 days at a temperature of 50 °C, this corresponding to a decrease of 38.7% referred to the value after preparation of the dispersion.

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### Example 6

A water-in-water polymer dispersion is prepared as in Example 4, except that the monomer solution contains 257.6 g water and 20.0 g fine citric acid powder are added after polymerisation.

The dispersion has a solution viscosity of 572 mPas and a salt viscosity of 226 mPas. The solution viscosity is 416 mPas after storage of the dispersion for a period of 55 days at a temperature of 50 °C, this corresponding to a decrease of 27.3% referred to the value after preparation of the dispersion.

### Comparative example 4

Example 4 was repeated, but without adding citric acid at any time.

The dispersion has a solution viscosity of 500 mPas and a salt viscosity of 208 mPas. The solution viscosity is 5 mPas after storage of the dispersion for a period of 55 days at a temperature of 50 °C, this corresponding to a decrease of 99% referred to the value after preparation of the dispersion.

### Example 7

A monomer solution is prepared, as described in Example 4. 2.0 g 30% hydrochloric acid are additionally mixed into the solution, which is polymerised in accordance with the procedure specified in Example 1. 5.0 g adipic acid are then mixed into the water-in-water polymer dispersion, which is then cooled in the manner described.

The dispersion has a solution viscosity of 708 mPas and a salt viscosity of 298 mPas.

The solution viscosity determined is 464 mPas after storage of the dispersion for a period of 45 days at a temperature of 50 °C, this corresponding to a decrease of 34.5% referred to the value after preparation of the dispersion.

**Example 8**

A monomer solution is prepared, as described in Example 4. 2.0 g 30% hydrochloric acid are additionally mixed into the solution, which is polymerised in accordance with the procedure specified in Example 1. 5.0 g benzoic acid are then mixed into the water-in-water polymer dispersion, which is then cooled in the manner described.

The dispersion has a solution viscosity of 768 mPas and a salt viscosity of 319 mPas.

The solution viscosity determined is 532 mPas after storage of the dispersion for a period of 45 days at a temperature of 50 °C, this corresponding to a decrease of 30.7% referred to the value after preparation of the dispersion.

**Example 9**

A monomer solution is prepared, as described in Example 4. 2.0 g 30% hydrochloric acid are additionally mixed into the solution, which is polymerised in accordance with the procedure specified in Example 1. 0.5 g 50% sulphuric acid are then mixed into the water-in-water polymer dispersion, which is then cooled in the manner described.

The dispersion has a solution viscosity of 716 mPas and a salt viscosity of 290 mPas.

The solution viscosity determined is 460 mPas after storage of the dispersion for a period of 45 days at a temperature of 50 °C, this corresponding to a decrease of 35.8% referred to the value after preparation of the dispersion.

**Example 10**

A monomer solution is prepared, as described in Example 4. 2.0 g 30% hydrochloric acid are additionally mixed into the solution, which is polymerised in accordance with the procedure specified in Example 1. 2.5 g acetic acid are then mixed into the water-in-water polymer dispersion, which is then cooled in the manner described.

The dispersion has a solution viscosity of 940 mPas and a salt viscosity of 395 mPas.

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The solution viscosity determined is 656 mPas after storage of the dispersion for a period of 45 days at a temperature of 50 °C, this corresponding to a decrease of 30.2% referred to the value after preparation of the dispersion.

#### Example 11

A monomer solution is prepared, as described in Example 4. 2.0 g 30% hydrochloric acid are additionally mixed into the solution, which is polymerised in accordance with the procedure specified in Example 1. 5.0 g citric acid are then mixed into the water-in-water polymer dispersion, which is then cooled in the manner described.

The dispersion has a solution viscosity of 780 mPas and a salt viscosity of 341 mPas.

The solution viscosity determined is 504 mPas after storage of the dispersion for a period of 45 days at a temperature of 50 °C, this corresponding to a decrease of 35.4% referred to the value after preparation of the dispersion.

#### Comparative example 5

A monomer solution is prepared, as described in Example 4. 2.0 g 30% hydrochloric acid are additionally mixed into the solution, which is polymerised and cooled in accordance with the procedure specified in Example 1.

The dispersion has a solution viscosity of 680 mPas and a salt viscosity of 287 mPas. The solution viscosity determined is 368 mPas after storage of the dispersion for a period of 45 days at a temperature of 50 °C, this corresponding to a decrease of 45.9% referred to the value after preparation of the dispersion.

#### Example 12

The procedure described in Example 11 is used, except that the monomer solution now contains 20.0 g sodium chloride instead of 20.0 g technical ammonium sulphate. The dispersion has a solution viscosity of 752 mPas and a salt viscosity of 302 mPas.

The solution viscosity determined is 568 mPas after storage of the dispersion for a period of 45 days at a temperature of 50 °C, this corresponding to a decrease of 24.5% referred to the value after preparation of the dispersion.

#### Example 13

The procedure described in Example 11 is used, except that the monomer solution now contains 20.0 g sodium sulphate · 10 H<sub>2</sub>O instead of 20.0 g technical ammonium sulphate. The dispersion has a solution viscosity of 976 mPas and a salt viscosity of 406 mPas.

The solution viscosity determined is 672 mPas after storage of the dispersion for a period of 45 days at a temperature of 50 °C, this corresponding to a decrease of 31.1% referred to the value after preparation of the dispersion.

#### Example 14

305.5 g fully demineralised water, 135.5 g 80% by weight trimethylammonium ethylacrylate chloride, 195.2 g 50% by weight acrylamide solution, 300.0 g 40% by weight polytrimethylammoniumpropylacrylamide chloride with a viscosity of the aqueous solution in the range of 150 to 300 mPas, 20.5 g polyethylene glycol with a molecular weight in the range of 9,000 to 12,000, 5.0 g technical ammonium sulphate and 2.0 g 5% by weight diethylenetriamine valeric acid sodium salt are put into a 2 l flask fitted with an agitator, a nitrogen supply line and a connection to a vacuum pump.

The pH of the solution is 5.0.

In accordance with the procedure specified in Example 1, the solution is freed of oxygen, heated to 40 °C and polymerised by adding 1 ml of a 5% by weight aqueous solution of sodium disulphate and 5 ml 0.01% by weight tertiary butyl hydroperoxide. If necessary, further small quantities of tertiary butyl hydroperoxide are subsequently added. After a maximum temperature of 56 °C has been reached, 5.0 g fine citric acid powder are mixed into the water-in-water polymer dispersion by stirring and the

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dispersion is then cooled to 20 °C while stirring constantly. The polymer content of the dispersion is 33.5% by weight.

The dispersion has a solution viscosity of 912 mPas and a salt viscosity of 151 mPas. The solution viscosity is 732 mPas after storage of the dispersion for a period of 42 days at a temperature of 50 °C, this corresponding to a decrease of 19.7% referred to the value after preparation of the dispersion.

#### Example 15

A water-in-water polymer dispersion is prepared as in Example 14, except that the monomer solution contains 300.5 g water and 10.0 g fine citric acid powder are added after polymerisation.

The dispersion has a solution viscosity of 1380 mPas and a salt viscosity of 225 mPas. The solution viscosity is 1410 mPas after storing the dispersion for a period of 42 days at a temperature of 50 °C.

#### Comparative example 6

Example 15 is repeated, the difference being that no citric acid is added after polymerisation.

The dispersion has a solution viscosity of 1240 mPas and a salt viscosity of 214 mPas. The solution viscosity is 256 mPas after storage of the dispersion for a period of 42 days at a temperature of 50 °C, this corresponding to a decrease of 79.4% referred to the value after preparation of the dispersion.

#### Application examples I – VIII

The respective flocculation values of the water-in-water dispersions obtained in accordance with Examples 1 and 2 and Comparative examples 1 and 2 were determined by the method described above, both immediately after preparation and after storage in closed containers for 20 days at 50 °C.

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The corresponding flocculation values in seconds are stated in Table I, below.

Table I

| Application example | Water-in-water dispersion according to                    | Flocculation value (s) |
|---------------------|---|------------------------|
| I                   | Example 1, day of preparation                             | 12.8                   |
| II                  | Example 1, after storage for 20 days at 50 °C             | 12.9                   |
| III                 | Comparative example 1, day of preparation                 | 12.6                   |
| IV                  | Comparative example 1, after storage for 20 days at 50 °C | 34.6                   |
| V                   | Example 2, day of preparation                             | 6.8                    |
| VI                  | Example 2, after storage for 20 days at 50 °C             | 7.2                    |
| VII                 | Comparative example 2, day of preparation                 | 7.0                    |
| VIII                | Comparative example 2, after storage for 20 days at 50 °C | 23.9                   |

Application examples IX A – XVI C

The water-in-water dispersions obtained in accordance with Examples 1 and 2 and Comparative examples 1 and 2 were used as drainage aids, both after preparation and after storage in a sealed container for 20 days at 50 °C. Their effect was determined in accordance with the above-mentioned Schopper-Riegler method.

The corresponding values are stated in Table II, below.

Table II

| Application example | Water-in-water dispersion according to        | Drainage time (s) |
|---------------------|---|-------------------|
| IX A                | Example 1, day of preparation                 | 98                |
| IX B                | Example 1, day of preparation                 | 79                |
| IX C                | Example 1, day of preparation                 | 61                |
| X A                 | Example 1, after storage for 20 days at 50 °C | 99                |
| X B                 | Example 1, after storage for 20 days at 50 °C | 77                |

|        |   |     |
|--------|---|-----|
| X C    | Example 1, after storage for 20 days at 50 °C             | 60  |
| XI A   | Comparative example 1, day of preparation                 | 96  |
| XI B   | Comparative example 1, day of preparation                 | 80  |
| XI C   | Comparative example 1, day of preparation                 | 61  |
| XII A  | Comparative example 1, after storage for 20 days at 50 °C | 122 |
| XII B  | Comparative example 1, after storage for 20 days at 50 °C | 118 |
| XII C  | Comparative example 1, after storage for 20 days at 50 °C | 90  |
| XIII A | Example 2, day of preparation                             | 82  |
| XIII B | Example 2, day of preparation                             | 60  |
| XIII C | Example 2, day of preparation                             | 50  |
| XIV A  | Example 2, after storage for 20 days at 50 °C             | 84  |
| XIV B  | Example 2, after storage for 20 days at 50 °C             | 60  |
| XIV C  | Example 2, after storage for 20 days at 50 °C             | 50  |
| XV A   | Comparative example 2, day of preparation                 | 83  |
| XV B   | Comparative example 2, day of preparation                 | 61  |
| XV C   | Comparative example 2, day of preparation                 | 51  |
| XVI A  | Comparative example 2, after storage for 20 days at 50 °C | 101 |
| XVI B  | Comparative example 2, after storage for 20 days at 50 °C | 82  |
| XVI C  | Comparative example 2, after storage for 20 days at 50 °C | 66  |

A, B, C stands for 0.01% by weight, 0.02% by weight and 0.03% by weight drainage aid on oven-dry material.

Application of the water-in-water dispersions obtained in accordance with Examples 3 to 15 and Comparative examples 3 to 6.

As indicated in Table III, the flocculation value (FV) of each of these water-in-water dispersions was determined by the method described above, both immediately after

preparation and after storage for 20 days in a sealed container at 25 °C (RT) or 50 °C. The drainage effect was also determined by the method described above after the specified storage.

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Table III

| Storage after ... days |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
|------------------------|------------------------|----------------------------|------------------|--------------------|------------|------------------------|----------------------------|------------------|-----------------|-------------|-------------|------------|----------|-------------------|----------------------------|------------------|--------------------|------------------|--|
| Ex. No.                | Salt viscosity [mPa's] | Solution viscosity [mPa's] | FV Stb II [sec.] | pH value 5% in FDW | Temp. [°C] | Salt viscosity [mPa's] | Solution viscosity [mPa's] | FV Stb II [sec.] | Pulp drainage * |             |             | Temp. [°C] | Days     | viscosity [mPa's] | Solution viscosity [mPa's] | FV Stb II [sec.] | pH value 5% in FDW | Viscosity drop % |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  | 0.05% [sec.]    | 0.1% [sec.] | 0.2% [sec.] |            |          |                   |                            |                  |                    |                  |  |
| 3                      | 210                    | 730                        | 4.8              | 3.0                | RT         | 232                    | 1040                       | 6.6              | 69              | 46          | 30          | RT         | appr. 60 | 225               | 854                        | 6.4              | 3.1                |                  |  |
| C3                     | 190                    | 700                        | 5.7              | 4.5                | RT         | 196                    | 704                        | 7.4              | 71.5            | 49          | 32          | RT         | appr. 60 | 214               | 808                        | 6.5              | 3.1                | 1.9              |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| 4                      | 248                    | 564                        | 7.3              | 3.7                | RT         | 155                    | 532                        | 7.4              | 73              | 49.5        | 33.5        | 40 °C      | appr. 60 | 136               | 456                        | 8                | 4.4                | -28.4            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| C4                     | 208                    | 500                        | 8.2              | 4.9                | RT         | 187                    | 436                        | 10.2             | 62.5            | 38          | 28          | 50 °C      | appr. 55 | 174               | 350                        | 12.4             | 4.8                | -45.4            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| 5                      | 227                    | 548                        | 7                | 3.3                | RT         | 214                    | 520                        | 6.8              | 74              | 46          | 30.5        | 50 °C      | appr. 55 | 217               | 520                        | 7.2              | 3.2                | -38.7            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| C5                     | 287                    | 680                        | 6.3              | 3.6                | RT         | 270                    | 636                        | 7                | 66              | 43.5        | 28          | 50 °C      | appr. 55 | 257               | 640                        | 6.7              | 3.5                | -45.9            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| 6                      | 228                    | 572                        | 6.7              | 3.1                | RT         | 226                    | 548                        | 7                | 70              | 49          | 29          | 50 °C      | appr. 55 | 225               | 532                        | 7                | 3.1                | -27.3            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| C6                     | 214                    | 1240                       | 8.5              | 4.2                | RT         | 198                    | 1150                       | 9.4              | 75              | 51          | 29          | 50 °C      | appr. 42 | 170               | 1110                       | 12.2             | 4.3                | -79.4            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| 7                      | 288                    | 708                        | 5.8              | 3.6                | RT         | 323                    | 732                        | 6.6              | 71              | 44          | 23          | 50 °C      | appr. 50 | 287               | 686                        | 6.5              | 3.7                | -34.5            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| 8                      | 319                    | 768                        | 5.8              | 3.7                | RT         | 332                    | 784                        | 6                | 70              | 41          | 24.5        | 50 °C      | appr. 45 | 315               | 768                        | 6.2              | 3.6                | -30.7            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| 9                      | 290                    | 716                        | 6.2              | 3.8                | RT         | 298                    | 708                        | 6.3              | 79.5            | 44          | 27          | 50 °C      | appr. 45 | 302               | 720                        | 8.2              | 3.5                | -35.8            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| 10                     | 395                    | 940                        | 5.4              | 3.7                | RT         | 402                    | 932                        | 5                | 82              | 46          | 26.5        | 50 °C      | appr. 45 | 408               | 928                        | 5.1              | 3.5                | -30.2            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| 11                     | 341                    | 780                        | 5.8              | 3.3                | RT         | 268                    | 740                        | 6.4              | 65              | 43          | 25.5        | 50 °C      | appr. 60 | 318               | 764                        | 6                | 3.3                | -35.4            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| 12                     | 302                    | 752                        | 6.3              | 3.4                | RT         | 302                    | 728                        | 6.5              | 70              | 44          | 24          | 50 °C      | appr. 50 | 308               | 772                        | 6.4              | 3.4                | -24.5            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
| 13                     | 408                    | 976                        | 5.2              | 3.4                | RT         | 426                    | 996                        | 4.8              | 89              | 42          | 21          | 50 °C      | appr. 50 | 404               | 968                        | 5                | 3.4                | -31.1            |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |
|                        |                        |                            |                  |                    |            |                        |                            |                  |                 |             |             |            |          |                   |                            |                  |                    |                  |  |

Table III

| Ex. No. | Storage after ... days    |                               |                     |                       |               |                           |                               |                     |                 |                |                |       |                           |                               |                     |                       |                         |  |
|---------|---------------------------|-------------------------------|---------------------|-----------------------|---------------|---------------------------|-------------------------------|---------------------|-----------------|----------------|----------------|-------|---------------------------|-------------------------------|---------------------|-----------------------|-------------------------|--|
|         | Salt viscosity<br>[mPa's] | Solution viscosity<br>[mPa's] | FV Stb II<br>[sec.] | pH value<br>5% in FDW | Temp.<br>[°C] | Salt viscosity<br>[mPa's] | Solution viscosity<br>[mPa's] | FV Stb II<br>[sec.] | Pulp drainage * |                |                | Days  | Salt viscosity<br>[mPa's] | Solution viscosity<br>[mPa's] | FV Stb II<br>[sec.] | pH value<br>5% in FDW | Viscosity drop =<br>[%] |  |
|         |                           |                               |                     |                       |               |                           |                               |                     | 0.05%<br>[sec.] | 0.1%<br>[sec.] | 0.2%<br>[sec.] |       |                           |                               |                     |                       |                         |  |
|         |                           |                               |                     |                       |               |                           |                               |                     |                 |                |                |       |                           |                               |                     |                       |                         |  |
| 14      | 151                       | 912                           | 12.3                | 3.4                   | RT            | 145                       | 910                           | 12.5                | 79              | 56             | 30             | RT    | 134                       | 944                           | 14.8                | 3.4                   |                         |  |
|         |                           |                               |                     |                       | 50 °C         | 135                       | 854                           | 13                  | 81              | 56             | 31             | 50 °C | 123                       | 732                           | 16.8                | 3.6                   | -19.7                   |  |
| 15      | 225                       | 1380                          | 8.1                 | 3.3                   | RT            | 200                       | 1260                          | 9.9                 | 73              | 48.5           | 26             | RT    | 202                       | 1240                          | 10.1                | 3.3                   |                         |  |
|         |                           |                               |                     |                       | 50 °C         | 200                       | 1560                          | 10.1                | 74              | 49             | 28             | 50 °C | 198                       | 1410                          | 13.6                | 3.3                   | 26.1                    |  |

FV = Flocculation value

Stb II = Stabiliser II

FDW = Fully demineralised water

\* = According to Schopper-Riegler

Temp. = Temperature during storage

RT = 25 °C

\*\* = Viscosity drop in the solution viscosity after preparation resulting from storage

C = Comparative example



**Patent claims**

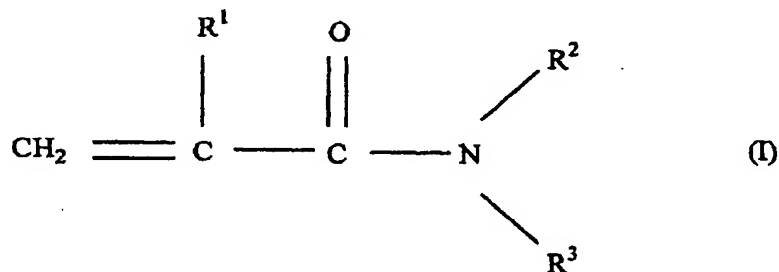
1. **Method for manufacturing a water-in-water polymer dispersion containing polymer A and at least one polymeric dispersant B, according to which monomers, which are dispersed in an aqueous phase containing water-soluble dispersant B, are subjected to radical polymerisation, possibly following the addition of a water-soluble salt, and, after polymerisation, a water-soluble acid is added to the water-soluble and/or water-swellaable polymer A obtained in this way, characterised in that the acid is added in quantities of 0.1 to 0.5% by weight and the salt in quantities of up to a maximum of 3% by weight, each referred to the total dispersion, where the total quantity of salt and acid amounts to a maximum of 5% by weight, referred to the total dispersion.**
  2. **Method as per Claim 1, characterised in that the acid is added in quantities of 0.2 to 3.5% by weight, preferably 0.3 to 2.0% by weight, referred to the total dispersion.**
  3. **Method as per Claim 1 or 2, characterised in that the salt is added in quantities of up to a maximum of 2.0% by weight, preferably 0.5 to 1.5% by weight, referred to the total dispersion.**
  4. **Method as per Claims 1 to 3, characterised in that the acid and the salt are added in a total quantity of a maximum of 3.5% by weight, referred to the total dispersion.**
  5. **Method as per Claims 1 to 4, characterised in that the water-soluble acid used is an organic acid and/or an inorganic acid, preferably an organic carboxylic acid, sulphonic acid, phosphonic acid and/or mineral acid.**
  6. **Method as per Claim 5, characterised in that the carboxylic acid used is an aliphatic or aromatic monocarboxylic, dicarboxylic, polycarboxylic acid and/or a hydroxycarboxylic acid, preferably acetic acid, propionic acid, citric acid, oxalic acid, succinic acid, malonic acid, adipic acid, fumaric acid, maleic acid, benzoic acid, particularly preferably citric acid, adipic acid and/or benzoic acid.**
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7. Method as per Claim 5, characterised in that the inorganic acid used is hydrochloric acid, sulphuric acid, nitric acid and/or phosphoric acid.
  8. Method as per Claims 1 to 7, characterised in that the water-soluble salt used is an ammonium, alkaline metal and/or alkaline-earth metal salt.
  9. Method as per Claim 8, characterised in that the inorganic salt used is an ammonium, sodium, potassium, calcium and/or magnesium salt.
  10. Method as per Claim 8 or 9, characterised in that the salt is a salt of an inorganic acid or an organic acid, preferably of an organic carboxylic acid, sulphonic acid, phosphonic acid or of a mineral acid.
  11. Method as per Claim 10, characterised in that the water-soluble salt is a salt of an aliphatic or aromatic monocarboxylic, dicarboxylic or polycarboxylic acid, a hydroxycarboxylic acid, preferably acetic acid, propionic acid, citric acid, oxalic acid, succinic acid, malonic acid, adipic acid, fumaric acid, maleic acid, benzoic acid, sulphuric acid, hydrochloric acid or phosphoric acid.
  12. Method as per Claim 11, characterised in that the water-soluble salt used is sodium chloride, ammonium sulphate and/or sodium sulphate.
  13. Method as per Claims 1 to 12, characterised in that the dispersant B used is a water-soluble polymer with a maximum  $M_w$  of  $2.0 \times 10^6$ , preferably 50,000 to  $1.2 \times 10^6$  g/mol, possibly mixed with a polyfunctional alcohol and/or a corresponding product of conversion with a fatty amine.
  14. Method as per Claim 13, characterised in that polymeric dispersant B contains at least one functional group selected from ether, carboxyl, sulphy, sulphate ester, amino, amido, imido, tertiary amino and/or quaternary ammonium groups.
  15. Method as per Claim 14, characterised in that polymeric dispersant B is a cellulose derivative, polyvinyl acetate, starch, starch derivative, dextran,
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polyvinylpyrrolidone, polyvinylpyridine, polyethylene imine, polyamine, polyvinylimidazole, polyvinyl succinimide, polyvinyl-2-methylsuccinimide, polyvinyl-1,3-oxazolidone-2, polyvinyl-2-methylimidazoline and/or their respective copolymer with maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, (meth)acrylic acid, salts of (meth)acrylic acid and/or a (meth)acrylic acid amide compound.

16. Method as per Claims 13 to 15, characterised in that dispersant B is a cationic polymer consisting of at least 30% by weight, preferably at least 50% by weight, particularly preferably 100% by weight, cationic monomer.
  17. Method as per Claim 16, characterised in that the cationic monomer is a diallyl dimethylammonium chloride, a dialkylaminoalkyl(meth)acrylate or dialkylaminoalkyl(meth)acrylamide with C<sub>1</sub>-C<sub>3</sub> in the alkyl or alkylene groups and protonated or quaternised as an ammonium salt, preferably the methyl chloride-quaternised ammonium salt of dimethylaminoethyl(meth)acrylate, dimethylaminopropyl(meth)acrylate or dimethylaminopropyl(meth)acrylamide, particularly preferably diallyl dimethylammonium chloride.
  18. Method as per Claims 13 to 17, characterised in that the polyfunctional alcohol used is a polyalkylene glycol, preferably polyethylene glycol, a block polymer of propylene/ethylene oxide with a molecular weight of 1,500 to 50,000, glycerin, ethylene glycol, propylene glycol, pentaerythritol and/or sorbitol.
  19. Method as per Claims 1 to 18, characterised in that polymeric dispersant B and the polyfunctional alcohol possibly present are added in quantities of 5 to 50% by weight, preferably 10 to 20% by weight, referred to the total dispersion.
  20. Method as per Claims 13 to 19, characterised in that the weight ratio of polymeric dispersant B to the polyfunctional alcohol is 1:0.01 to 0.5, preferably 1:0.01 to 0.3.
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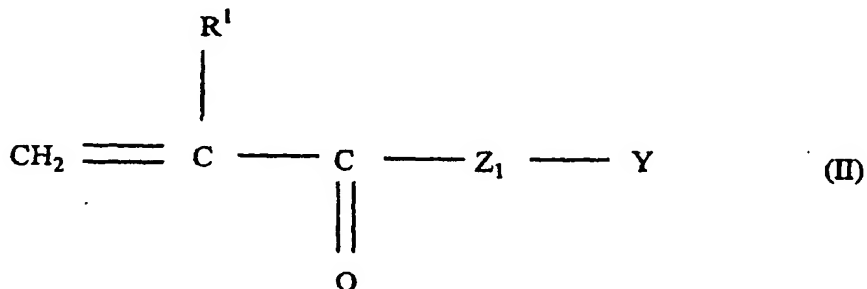
21. Method as per Claims 1 to 20, characterised in that polymer A has an  $M_w$  of  $> 1.0 \times 10^6$  g/mol.
22. Method as per Claims 1 to 21, characterised in that polymer A is made up of non-ionic and/or cationic and/or amphiphilic, ethyleneically unsaturated, preferably water-soluble monomers, where the content of water-insoluble monomers possibly present is selected so as not to impair the water-solubility or water-swellability of polymer A.
23. Method as per Claim 22, characterised in that the non-ionic monomers used are compounds of general formula (I)



where

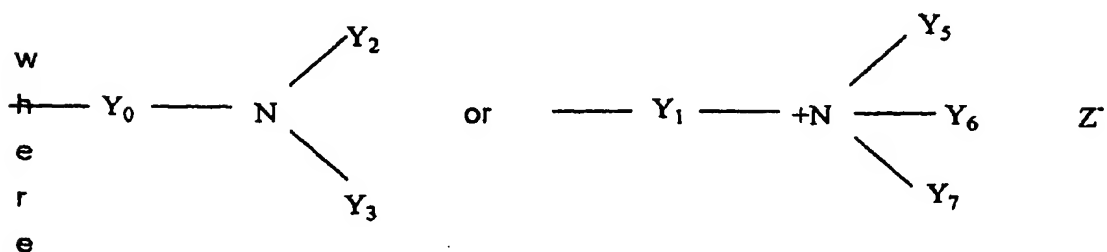
$\text{R}^1$  stands for hydrogen or a methyl residue, and  
 $\text{R}^2$  and  $\text{R}^3$  stand, independently of each other, for hydrogen, for an alkyl or hydroxyalkyl residue with 1 to 5 C atoms,

the cationic monomers used are compounds of general formula (II)



where

- $R^1$  stands for hydrogen or a methyl residue,  
 $Z_1$  stands for O, NH or  $NR_4$  with  $R_4$  for an alkyl residue with 1 to 4 C atoms, and  
 $Y$  for one of the groups

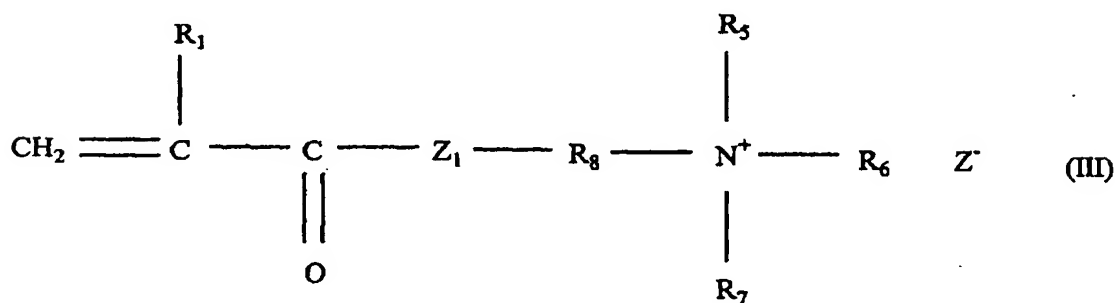


$Y_0$  and  $Y_1$  stand for an alkylene residue, possibly substituted with hydroxy groups, with 2 to 6 C atoms,

$Y_2, Y_3, Y_4, Y_5, Y_6, Y_7$ , independently of each other, stand for an alkyl residue with 1 to 6 C atoms, and

$Z^-$  stands for halogen, acetate,  $SO_4CH_3^-$ ,

and the amphiphilic monomers are compounds of general formula (III) or (IV)

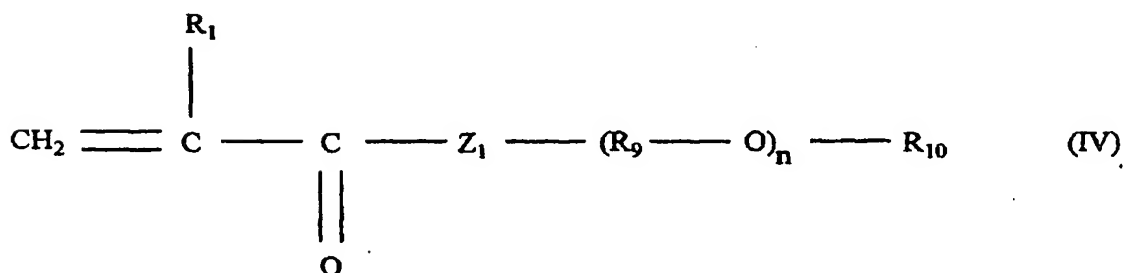


where

- $Z_1$  stands for O, NH,  $NR_4$  with  $R_4$  for an alkyl residue with 1 to 4 carbon atoms,

- $R_1$  stands for hydrogen or a methyl residue,  
 $R_8$  stands for an alkylene residue with 1 to 6 carbon atoms,  
 $R_5$  and  $R_6$  stand, independently of each other, for an alkyl residue with 1 to 6 carbon atoms,  
 $R_7$  stands for an alkyl, aryl and/or aralkyl residue with 8 to 32 carbon atoms, and  
 $Z$  stands for halogen, pseudo-halogen,  $SO_4CH_3^-$  or acetate,

or



where

- $Z_1$  stands for O, NH,  $NR_4$  with  $R_4$  for an alkyl residue with 1 to 4 carbon atoms,  
 $R_1$  stands for hydrogen or a methyl residue,  
 $R_{10}$  stands for hydrogen, an alkyl, aryl and/or aralkyl residue with 8 to 32 carbon atoms,  
 $R_9$  stands for an alkylene residue with 2 to 6 carbon atoms,  
 and  
 $n$  stands for an integer between 1 and 50.

24. Method as per Claim 22 or 23, characterised in that polymer A is made up of 1 to 99% by weight, preferably 20 to 80% by weight, cationic monomers

25. Method as per Claims 1 to 24, characterised in that polymer A is present in quantities of 5 to 60% by weight, preferably 10 to 50% by weight, referred to the total dispersion.
  26. Method as per Claims 1 to 25, characterised in that, for radical polymerisation, the initiator system is added continuously during the entire course of polymerisation.
  27. Water-in-water polymer dispersion obtainable by one or more of Claims 1 to 26.
  28. Use of the water-in-water polymer dispersion as per Claim 27 as a flocculant in the sedimentation of solids, preferably in the conditioning of water and process water or in waste water treatment, in raw materials extraction, preferably coal, aluminium or petroleum, as an auxiliary in papermaking or as a demulsifier in the separation of water mixtures containing oil and/or fat.
  29. Use of the water-in-water polymer dispersion as per Claim 27 as a thickener.
  30. Use of the water-in-water polymer dispersion as per Claim 27 as a retention agent and drainage aid in papermaking.
  31. Use of the water-in-water polymer dispersion as per Claim 27 as an additive for a crop protection agent, possibly together with other biologically effective substances.
  32. Use of the water-in-water polymer dispersion as per Claim 27 as an additive for an anti-erosion agent.
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Figure 1/1

